

Conference Paper

Limestone Addition Effect on Phase Composition of Red Mud Reduction Roasting Products

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There are millions of tons of solid waste residues accumulated in present-day alumina industry. Those solid waste residues contain red mud and belit mud. The creation of sludge depository, its keeping and taking environmental protection measures cost up to \$8-12 million a year. However, red mud is a valuable raw material. The extraction of some useful elements from red mud makes it possible to obtain such valuable products as pig iron, iron-bearing concentrate, rare-earth elements, alumina concrete, constructional materials, etc.

The current state of technological, technical and economic research in the pyrometallurgy of red mud is reflected in the works [1-3] which show that despite the considerable experience in complex processing of red mud by pyrometallurgical methods, none of them has been extensively used. The efficiency of red mud complex processing can be enhanced by the number increasing of useful products obtained and by reducing the proportion of mud sent to pyrometallurgical conversion.

In some other works, solutions for the processing of red mud are presented either by reduction melting using the smelting furnace [4-6] or rotary furnace with subsequent processing by the Bayer process and enrichment [6]. Some works also indicate that at the end of pyrometallurgical conversion there are two products - the foundry iron and slag which can further be used in the alumina or cement clinker production. However, abundant impurities in the red mud prevent the production of high-quality iron and alumina concrete. In particular, a pig iron may contain a considerable amount

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Component	Content, mass. %								Sum
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Other	$\Delta m_{\text{calcination}}$	
Microcalcite (CaCO ₃)	56,35	0,04	0,06	0,04	0,02	0,01	0,01	43,46	100
Red mud*	12,1	8,99	12,55	44,89	2,5	0,7	11,53	6,74	100
Coke fine	0,00	0,00	0,00	0,00	0,00	0,00	1,10	98,90**	100

TABLE 1: The chemical composition of raw mixture components. * - leached ** - carbon.

of sulfur and phosphorous, and the alumina concrete may contain alkaline, mayenit ($12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$) and gelenit ($\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10}$).

It is pointed out in [7] that sulfur and phosphorus oxides can form solid solutions with silicate phases of Portland cement such as alit ($3\text{CaO} \cdot \text{SiO}_2$ or C_3S) and belit ($2\text{CaO} \cdot \text{SiO}_2$ or C_2S) and the oxides can be absorbed by them during the reduction roasting of Portland clinker.

We have proposed to carry out the reduction roasting of red mud with the simultaneous correction of roasting product phase composition by the addition of calcium carbonate and carbonaceous reducing agent into the raw mixture. During the reduction roasting calcium carbonate forms aluminosilicate phases absorbing phosphorus and sulfur oxides. Such an approach allows converting impurities harmful to pig iron into aluminosilicate phases and obtaining pure iron during further separation of silicate and iron-containing roasting products.

The present work was focused on the type and number determination of phases formed under the conditions of red mud reduction roasting in accordance with the CaCO_3 amount. The possibility of Portland clinker and pig iron obtaining on the basis of roasting products after silicate and iron separation was also studied.

The chemical composition of raw mixture components is presented in Table 1.

The raw mixtures composition is given in Table 2.

The raw components were dried and homogenized by co-grinding for 30 minutes in a laboratory mill. The homogenized mixture was wetted to optimal moisture and pressed at 300 MPa. The pressed samples were roasted to 1100°C in a muffle furnace without isothermal exposure. The reduction roasting products were studied by X-ray diffraction analysis (XDA). The quantitative X-ray phase analysis was performed with STADI-P diffractometer (STOE, Germany).

Figure 1 shows the XRD data of the original red mud (a) and XRD data of reduction roasting products of a raw mix containing 10 mass. % CaCO_3 (b).

The composition and amount of reduction roasting products are given in Table 3.

The name of the raw mixture	The component amount in the raw mixture, mass. %		
	CaCO ₃	Red mud	Coke fine (over 100 %)
Original red mud	0	100,0	0
The raw mixture containing 10 mass. %CaCO ₃	10,0	90,0	7,5
The raw mixture containing 20 mass. %CaCO ₃	20,0	80,0	7,5
The raw mixture containing 30 mass. %CaCO ₃	30,0	70,0	7,5
The raw mixture containing 40 mass. %CaCO ₃	40,0	60,0	7,5

TABLE 2: The raw mixtures composition.

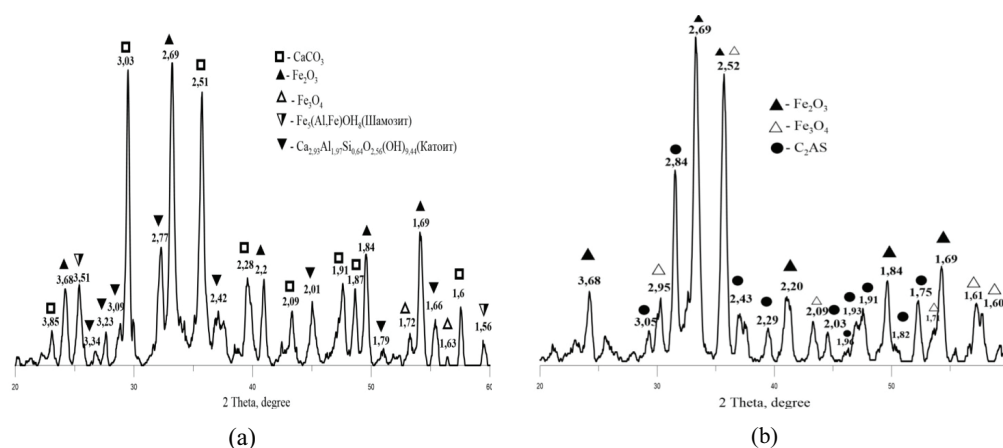


Figure 1: The XRD data of the original red mud (a) and XRD data of reduction roasting products of a raw mix containing 10 mass. % CaCO₃ (b).

Table 3 shows that reduction roasting of raw mixtures with different CaCO₃ addition allows removing iron oxides from complex iron-containing compounds (chamosite) into independent oxide iron-containing phases. The optimal value is 10 mass % CaCO₃ in the raw mixture. If it is more than 10 mass %, complex iron-silicate compounds are formed in reduction roasting products which cannot be separated by mechanical enrichment methods into silicate concentrate and iron-containing concentrates.

The raw mixture with 10 mass % CaCO₃ was roasted in reductive conditions to obtain the metallic iron based on iron-containing oxides. Fig. 2 shows the XRD data of products obtained during reductive roasting to the metallic iron.

Raw mixture composition	Phase content, mass. %							Sum
	CaCO ₃	Chamosite	Katoite	Gelenit	Fe ₂ O ₃	Fe ₃ O ₄	Other	
Original red mud	25,9	8,33	15,12	0	39,5	0	11,15	100
Red mud + 10 mass. % CaCO ₃	0	0	0	29,44	50,15	11,04	9,37	100
	Phase content, mass. %							
Raw mixture composition	C ₂ MF*	Ca _{1,5} Fe _{3,4} Si ₃ O	Fe ₂ O ₃	Fe ₃ O ₄	C ₄ AF**	C ₂ S, C ₃ S	Other	
Red mud + 20 mass. % CaCO ₃	16,8	7,31	53,75	13,89	0	0	8,25	100
Red mud + 30 mass. % CaCO ₃	0	0	25,64	8,064	46,45	19,83	0,016	100
Red mud + 40 mass. % CaCO ₃	0	0	10,83	7,19	16,67	65,29	0,02	100

TABLE 3: The composition and amount of reduction roasting products. * - Ca₂Mg·Fe₂O₆ ** - 4CaO·Al₂O₃·Fe₂O₃.

C	Mn	Si	P	S	Cu + Cr + Ni + Sn + Mo
4,31-5,17	0,71-0,80	2,47-4,94	0,74-0,84	0,005-0,013	0,152-0,238

TABLE 4: The chemical composition of pig iron obtained from three experimental meltings.

Figure 2 also demonstrates that small amount of perovskite (CaO·TiO₂) was found in reduction roasting products in addition to metallic iron and gelenit. The next raw mixture calculations for the Portland cement clinker production should take into consideration this small amount of perovskite. Tamman's furnace was used to perform an oxidative separative melting of products obtained during the reductive roasting to the metallic iron of raw mixture with 10 mass %CaCO₃. Pig iron and gelenit slag were formed at the end of melting. The chemical composition of pig iron is given in Table 4.

The impurities content varies from melting to melting (Table 4) and, therefore, it should be investigated in further experiments for optimal melting conditions and for

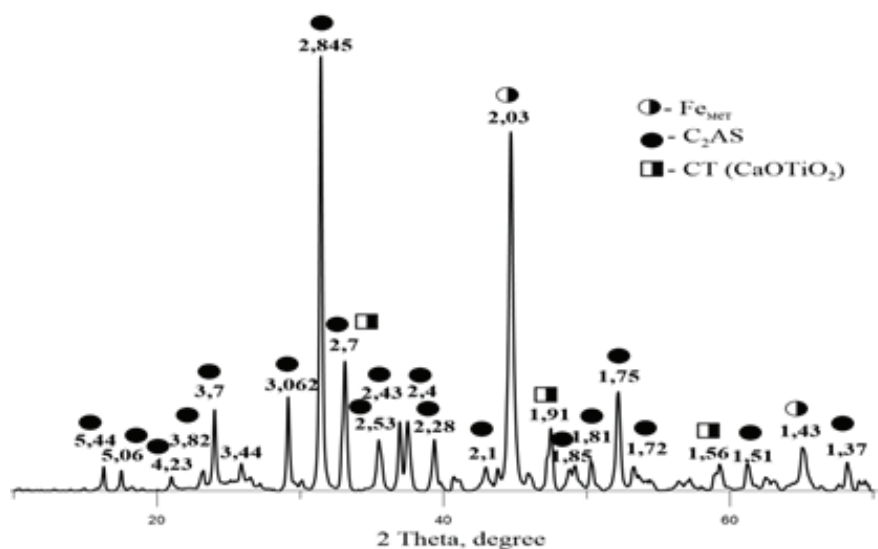


Figure 2: The XRD data of products obtained during the reductive roasting to the metallic iron of raw mixture with 10 mass %CaCO₃.

the limitation of impurities reduction under conditions of low temperature and lack of reducing agent. As the non-ferrous impurities are hardly oxidized and cannot be practically removed, their content is low and corresponds to the range of pure raw materials (Table 5). It allows using the pig iron in the production of national steel grades with special permissions of non-ferrous impurities content (Table 6). In general, the final pig iron obtained in our experiment meets the requirements of normative documents.

According to the standard procedure, a raw mixture based on gellenite slag was calculated for production of a typical Portland cement clinker with modular characteristics $KH = 0,92$; $n = 2,3$ и $p = 1,6$. The mixture was then roasted in a muffle furnace at 1400°C. The obtained Portland clinker was grinded with gypsum to a normative grade.

The physico-mechanical properties of produced Portland clinker are in good agreement with normative requirements.

1. Conclusions

The experimental results show that the developed technology can be used for complex red mud utilization with simultaneous output of several high-quality products.

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Material type	Cu + Cr + Ni + Sn + Mo
Direct-reduced iron	0,02
Pig iron	0,06
Home scrap: Busheling scrap Capital scrap	0,13 0,20
Bought scrap: Milled automotive Heavy obsolete Packed obsolete	0,51 0,70 1,00

TABLE 5: The content of non-ferrous impurities difficult to remove in the general grades of steelmaking raw materials.

Material type	Cu + Cr + Ni + Sn + Mo
Cold-rolled steel for automobile production	<0,13
Cold-rolled drawing quality steel	<0,15
Massive plate, railings	<0,20
Hot-rolled steel, standard list of steel	<0,40
Rolled steel, rods	<0,50
Rebar	<0,80

TABLE 6: The impurity content allowances in the different grades of steel.

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